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Direct N- and C-alkenylation of nitrogen-containing heterocycles with magnesium alkylidene carbenoids

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Abstract—Treatment of magnesium alkylidene carbenoids, which were generated from 1-chlorovinyl *p*-tolyl sulfoxides with isopropylmagnesium chloride at −78 °C in toluene, with *N*-lithio nitrogen-containing heterocycles gave *N*-alkenylated products in moderate to good yields. Also, the reaction of *C*-lithio indoles, which were generated from *N*-protected indoles, with magnesium alkylidene carbenoids gave *C*-2 or *C*-3 alkenylated products, corresponding to the protective group. The intermediate of these reactions were found to be the alkenyl anion, which could be trapped with electrophiles to give the heterocycles having fully substituted alkenes.

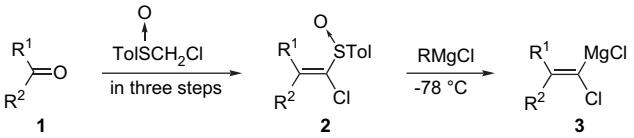
1. Introduction

Nitrogen-containing heterocycles are undoubtedly one of the most important fundamentals in organic chemistry. They are widely distributed in natural products and in pharmaceuticals, and numerous studies for their chemistry and synthesis have been reported. From the synthetic point of view, direct N- and C-alkenylation of nitrogen-containing heterocycles are not an easy task.

Though some examples were reported to synthesize *N*-alkenylated nitrogen-containing heterocycles,[1] it required higher temperature than ambient temperature or sonication[1i] except our previous communication.[2] The *N*-alkenylated nitrogen-containing heterocycles are useful intermediates in a wide range of reactions and in polymer science.[1n] Otherwise, the vinyl group could be used as a protecting group.[3] From these background, novel methods to synthesize *N*-alkenylated nitrogen-containing heterocycles are still an important task in organic chemistry.

For C-alkenylation of nitrogen-containing heterocycles, fewer examples are reported than N-alkenylation.[4,1l] Furthermore, all of the examples reported were unable to alkenylate the nitrogen atom, *C*-2, and *C*-3 carbon selectively, though regioselective alkenylation of *C*-2 and *C*-3 carbon of indoles and pyrroles were reported.[4c,e,g,h]

Alkylidene carbenes and carbenoids are an interesting and highly reactive carbon species and numerous studies were reported about the generation and reactivity of them.[5] Recently, we reported a new method for generation of magnesium alkylidene carbenoids **3** from 1-chlorovinyl *p*-tolyl sulfoxides **2**,[6] which were synthesized from ketones **1** and chloromethyl *p*-tolyl sulfoxide in three steps in high yields[6,7] with a Grignard reagent via a sulfoxide–magnesium exchange reaction (Scheme 1).[6,8] From the generated magnesium alkylidene carbenoid **3**, some new methods, especially reactions with various nucleophiles were recently established by our group.[6,9]



Scheme 1. Generation of magnesium alkylidene carbenoid **3**.

In continuation of our interest in the development of new synthetic methods by utilizing the generated magnesium alkylidene carbenoids **3**, we found that the reaction with *N*-lithio nitrogen-containing heterocycles gave *N*-alkenylated products **5** (E=H) in moderate to good yields (Scheme 2).[2] Also, we found that the intermediate of the reaction was the alkenyl anion **4**, which could be trapped with various electrophiles to afford **5** (E=substituent). Furthermore, in order to expand the scope of this procedure, we studied about the reaction of **3** with lithiated *N*-protected indoles to produce *C*-alkenylated products. In this paper the details of the results are reported.

Keywords: Sulfoxide–magnesium exchange reaction; Magnesium alkylidene carbenoid; Alkenylation; N-Alkenylation of heterocycles; C-Alkenylation of heterocycles.
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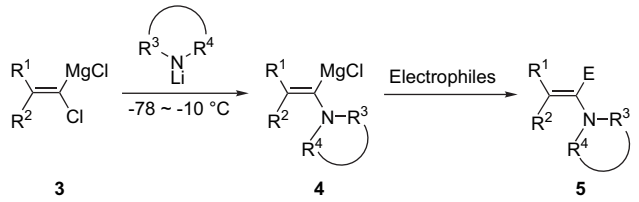


Scheme 2. Synthesis of *N*-alkenylated nitrogen-containing heterocycles **5**.

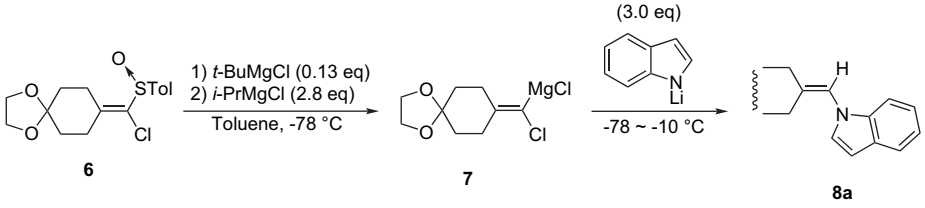
2. Results and discussion

2.1. Direct N-alkenylation of *N*-lithio nitrogen-containing heterocycles with magnesium alkylidene carbenoid 7

1-Chlorovinyl *p*-tolyl sulfoxide **6**, which was synthesized from 1,4-cyclohexanedione monoethylene ketal and chloromethyl *p*-tolyl sulfoxide in high yield,[6b] in dry toluene was treated with *t*-BuMgCl (0.13 equiv) at −78 °C to remove a trace of moisture in the reaction mixture.[9a,b] After 10 min, *i*-PrMgCl (2.8 equiv) was added to the reaction mixture. The sulfoxide–magnesium exchange reaction took place instantaneously to give the magnesium alkylidene carbenoid **7**. Subsequently, 3 equiv of *N*-lithio indole, which was generated from indole and *n*-BuLi was added via cannula to the generated carbenoid **7**. The reaction mixture was allowed to warm to −10 °C to afford *N*-alkenylated indole **8a** in 54% yield (Scheme 3).

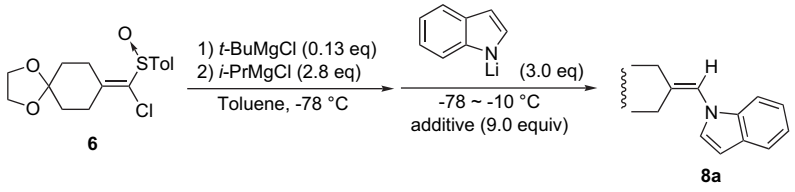
Because we recognized that this is quite interesting and novel reaction, improvement of the yield was undertaken and results are summarized in Table 1. The use of THF and cyclopentyl methyl ether (CPME) as the solvent did not improve the yield (entries 2 and 3). Diethyl ether could not be applied as a solvent because 1-chlorovinyl *p*-tolyl sulfoxide did not dissolve in diethyl ether at −78 °C. Next, we investigated the effect of additives. CPME, HMPA, DME, 1,4-dioxane, and 12-crown-4-ether did not improve the yield (entries 4–8). Finally, when *N*-lithio indole was prepared with 9 equiv of diethyl ether (corresponding to 1-chlorovinyl *p*-tolyl sulfoxide **7**) the best result was obtained with slight improvement of the yield compared with only toluene used as the solvent (entry 9). So we decided the condition in entry 9 as the optimized condition.

Next, we investigated the reaction of the magnesium alkylidene carbenoid **7** with other *N*-lithio nitrogen-containing heterocycles under the optimized condition described above and the results are summarized in Table 2. The reaction with indazole gave the desired *N*-alkenylated product **8b** in 51% yield (entry 1); however, pyrazole gave only 15% yield of the desired product **8c** (entry 2). Phenothiazine and phenoxazine gave quite good yields of the *N*-alkenylated products **8d** and **8e** (entries 3 and 4). Interestingly, carbazole, expected to be quite similar compound with phenoxazine and phenothiazine, gave only complex mixture in this reaction (entry 5). In contrast to the results described above, the simplest nitrogen-containing heterocycles, pyrrole gave 2-alkenylated pyrrole **8g** as a main product in 56% yield with *N*-alkenylated pyrrole **8f** in only 14% yield (entry 6). 2,5-Dimethylpyrrole gave only the desired *N*-alkenylated product **8h** in 54% yield (entry 7).



Scheme 3. Synthesis of *N*-alkenylated indole **8a**.

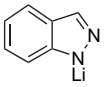
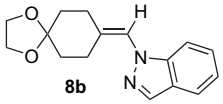
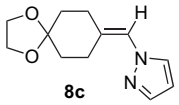
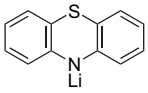
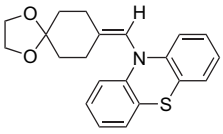
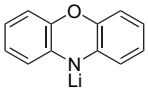
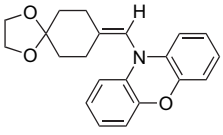
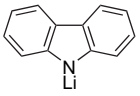
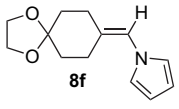
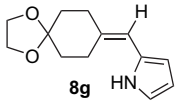
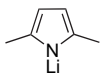
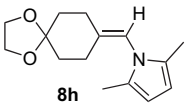
Table 1. Conditions for the synthesis for *N*-alkenylated indole **8a**



Entry	Solvent	Additive	Yield of **8a**/%
1	Toluene	None	54
2	THF	None	46
3	CPME[a]	None	39
4	Toluene	CPME[a]	56
5	Toluene	HMPA	43
6	Toluene	DME	32
7	Toluene	1,4-Dioxane	56
8	Toluene	12-Crown-4-ether	2
9	Toluene	Diethyl ether	57

[a] CPME: cyclopentyl methyl ether.

Table 2. The direct N-alkenylation of nitrogen-containing heterocycles with magnesium alkylidene carbenoid **7**

Entry	*N*-Lithio nitrogen-containing heterocycle	*N*-Alkenylated heterocycle **8**	Yield/%
1		 **8b**	51
2		 **8c**	15
3		 **8d**	71
4		 **8e**	70
5		—[a]	
6		 **8f**	14
		 **8g**	56
7		 **8h**	54

[a] A complex mixture was obtained.

2.2. Trapping the intermediate 9 with electrophiles

Based on our previous studies,[6b] the intermediate of this reaction was thought to be the alkenyl anion. To ascertain that the intermediate was the alkenyl anion, the reaction between the magnesium alkylidene carbenoid **7** and *N*-lithio phenothiazine was quenched with CH_3OD. This reaction gave the deuterated *N*-alkenylated product **10a** in 71% yield with 98% deuterium incorporation (see Table 3, entry 1). From this result, it was confirmed that the existence of the alkenyl anion **9** as the intermediate of this reaction.

We thought that if this alkenyl anion intermediate **9** could be trapped with electrophiles, a novel method for a synthesis of nitrogen-containing heterocycles bearing fully substituted olefin on the nitrogen atom would be realized. At the point of our previous communication,[2] our method was the only way to synthesize such an olefin, though Movassaghi et al. reported a method of synthesizing nitrogen-containing heterocycles bearing fully substituted olefin on the nitrogen atom[1v] after our communication. First, 9 equiv of iodomethane was added to the reaction mixture at −10 °C and the reaction was allowed to warm to room temperature and was stirred for 1 h; however, no expected methylated product was obtained. Next, 5 mol % of copper iodide[10] followed by 9 equiv of iodomethane was added to the reaction mixture at −10 °C and the reaction was warmed to room temperature, and run for 1 h. To our delight, this reaction gave the desired methylated product **10b** in 62% yield (entry 2).

The results of trapping the intermediate **9** with several electrophiles are summarized in Table 3. The reaction with iodoethane turned out to be sluggish; but loading 20 mol % of copper iodide with prolonging the reaction time to 6 h gave the ethylated product in moderate yield (entry 3). Reaction with allyl iodide gave the desired product in good yield; though isopropyl iodide did not give any of the desired product but only the protonated product **8d** even in modified condition used in the reaction with iodoethane (entries 4 and 5). Reaction with benzyl bromide gave the desired product in only 30% yield; the TLC analysis showed many byproducts (entry 6).

Next, we applied carbonyl compounds as electrophiles. Benzoyl chloride and phenyl isocyanate gave desired products (entries 7 and 8). Acetaldehyde and acetone did not react at all with the alkenyl anion **9** (entries 9 and 10). These results suggest that the nucleophilicity of the anion **9** is not enough to react with aliphatic ketones and aldehydes.

2.3. Generality and stereochemistry of the reaction between 1-chlorovinyl *p*-tolyl sulfoxides and *N*-lithio indole

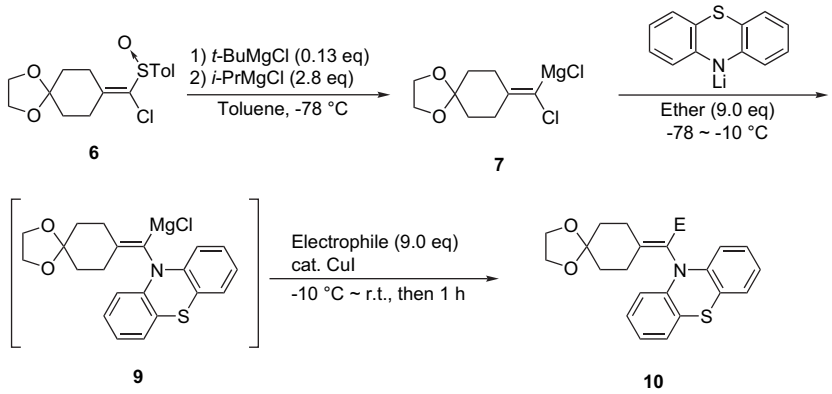
Generality and stereochemistry of the reaction was studied using various 1-chlorovinyl *p*-tolyl sulfoxides. First, symmetrical 1-chlorovinyl *p*-tolyl sulfoxides, which were derived from cyclopentadecanone, cyclohexanone, and acetone, were applied and results are summarized in Table 4. It shows that this reaction could be generally applied to other 1-chlorovinyl *p*-tolyl sulfoxides; however, in these cases, the yields were found to be moderate.

Next, we investigated the stereochemistry of the reaction using unsymmetrical 1-chlorovinyl *p*-tolyl sulfoxides as the substrates. The results of the reaction between unsymmetrical 1-chlorovinyl *p*-tolyl sulfoxides and *N*-lithio indole are summarized in Table 5. According to our previous report;[9e] including theoretical studies of magnesium alkylidene carbenoid, high stereoselectivity or stereospecificity was expected. Also, some reports studied about the stereochemistry of alkylidene carbenoids[11] supported our hypothesis. But contrary to our expectation, no particularly notable stereoselectivity or stereospecificity was observed though slight stereospecificity was observed when 1-chlorovinyl *p*-tolyl sulfoxide derived from 2-cyclohexenone or methyl vinyl ketone was applied as the substrate (entries 1–4).

2.4. Direct alkenylation at the *C*-2 and *C*-3 carbon of the indole ring

It is known that nitrogen-protected indoles will be lithiated at the *C*-2 or *C*-3 carbon, corresponding to the protective

Table 3. Trapping the intermediate **9** with electrophiles



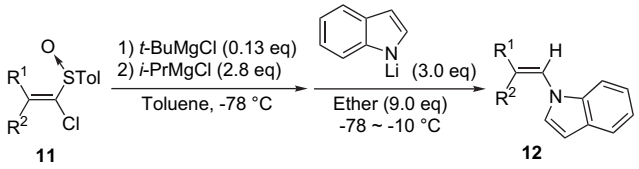
6 **7** **9** **10**

Entry	Electrophile	CuI/mol %	E	Yield of **10**/%
1	CH_3OD	None	–D	**10a**, 71[a]
2	CH_3I	5	$–CH_3$	**10b**, 62
3	CH_3CH_2I	20	$–CH_3CH_2$	**10c**, 55[b]
4	$CH_2{=}CHCH_2I$	5	$–CH_2CH{=}CH_2$	**10d**, 63
5	$(CH_3)_2CHI$	5	$–CH(CH_3)_2$	—
6	$PhCH_2Br$	5	$–CH_2Ph$	**10e**, 30
7	PhCOCl	None	–COPh	**10f**, 59
8	PhNCO	None	–CONHPh	**10g**, 39
9	CH_3CHO	None	$–CH(CH_3)OH$	—
10	$(CH_3)_2CO$	None	$–C(CH_3)_2OH$	—

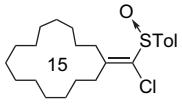
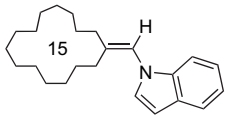
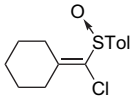
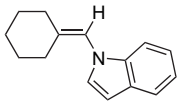
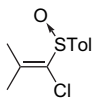
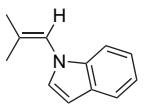
[a] Deuterium content 98%.
[b] The reaction mixture was stirred for 6 h at room temperature.

group.[12] We investigated to apply nitrogen-protected indoles as nucleophiles for the magnesium alkylidene carbenoid. First, we studied for direct *C*-2 alkenylation. To prepare *C*-2 lithio indole, we used *N*-methyl indole first. Using *N*-methyl-2-lithio indole as a nucleophile, we obtained *C*-2 alkenylated indole **13a** though the yields were not satisfactory (Scheme 4). Even though the yield was low, we were delighted because no product, which was alkenylated at the other position of indole was obtained.

Table 4. Generality of the reaction of 1-chlorovinyl *p*-tolyl sulfoxides **11** with *N*-lithio indole



11 **12**

Entry	1-Chlorovinyl *p*-tolyl sulfoxide	*N*-Alkenylated indole	Yield of **12**/%
1	 **11a**	 **12a**	44
2	 **11b**	 **12b**	46
3	 **11c**	 **12c**	46

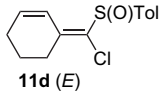
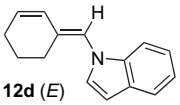
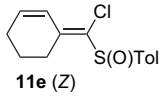
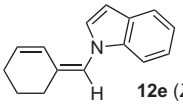
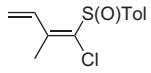
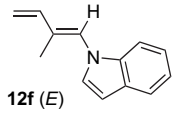
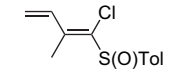
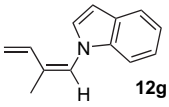
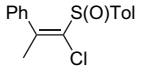
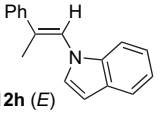
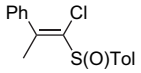
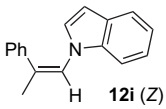
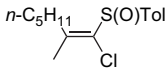
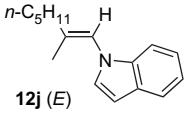
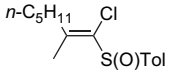
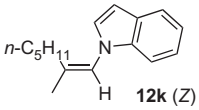
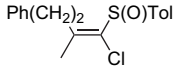
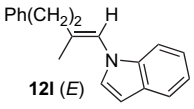
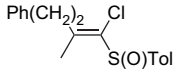
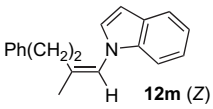
Next, in order to confirm the presence of the alkenyl anion as the intermediate, we quenched the reaction between magnesium alkylidene carbenoid **7** and *N*-PMP-2-lithio indole with CH_3OD. This reaction gave the deuterated compound **15** with 74% deuterium incorporation (Table 7, entry 1). Anyway, we were able to confirm the existence of the alkenyl anion **14**.

Then, we investigated the reactivity of the alkenyl anion **14** by trapping it by electrophiles. The results are summarized

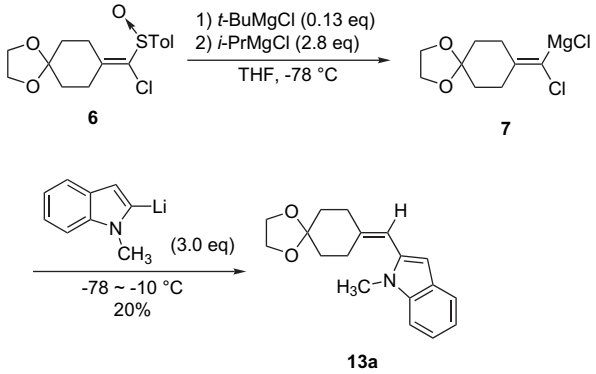
To improve the yield, we applied other protected indoles such as *N*-phenylsulfonyl indole,[13] *N*-Boc indole, *N*-SEM indole,[12a] and *N*-PMP indole;[14] which were prepared by known procedure. The results of *C*-2 alkenylation of indole are summarized in Table 6.

N-Phenylsulfonyl indole and *N*-Boc indole showed slight improvement of yield (entries 1 and 2), but *N*-SEM indole showed lower yield than *N*-methyl indole (entry 3). Through the investigation, THF was used as solvent because 2-lithio indole could not be prepared in other solvents such as toluene and ether. Finally, we found that *N*-PMP indole gave the desired 2-alkenylated indole in moderate yield. As a modified condition, toluene was used to generate magnesium alkylidene carbenoid **7** when *N*-PMP indole was used (entry 4). Although, this condition was applied to other *N*-protected indoles, no improvement of the yield was observed. In addition, any product, which was alkenylated at the other position of indole was not obtained in all the cases.

Table 5. Stereochemistry of the reaction between unsymmetrical 1-chlorovinyl *p*-tolyl sulfoxides and *N*-lithio indole

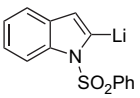
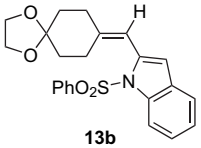
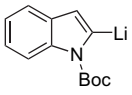
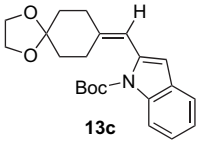
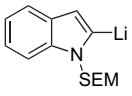
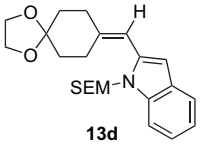
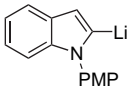
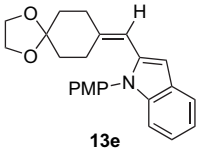
Entry	1-Chlorovinyl *p*-tolyl sulfoxide	*N*-Alkenylated indole	*E*/*Z*[a]	Yield of **12**/%
1	 **11d** (*E*)	 **12d** (*E*)	27/73	37
2	 **11e** (*Z*)	 **12e** (*Z*)	80/20	30
3	 **11f** (*E*)	 **12f** (*E*)	32/68	31
4	 **11g** (*Z*)	 **12g** (*Z*)	78/22	30
5	 **11h** (*E*)	 **12h** (*E*)	33/67	25
6	 **11i** (*Z*)	 **12i** (*Z*)	81/19	43
7	 **11j** (*E*)	 **12j** (*E*)	42/58	48
8	 **11k** (*Z*)	 **12k** (*Z*)	56/44	46
9	 **11l** (*E*)	 **12l** (*E*)	29/71	65
10	 **11m** (*Z*)	 **12m** (*Z*)	44/56	64

[a] The ratio of *E*/*Z* was determined from their ^{1}H NMR.



Scheme 4. Reaction of *N*-methyl-2-lithio indole with magnesium alkylidene carbenoid **7**.

Table 6. Reaction of *N*-protected indoles with magnesium alkylidene carbenoid **7**

Entry	*N*-Protected 2-lithio indole[a]	2-Alkenylated indole	Yield of **13**/%
1		 **13b**	33
2		 **13c**	24
3		 **13d**	15
4[b]		 **13e**	44

[a] Boc=*tert*-butoxy carbonyl, SEM=2-trimethylsilylethoxymethyl, PMP=*p*-methoxyphenyl.
[b] Toluene was used as solvent to generate magnesium alkylidene carbenoid **7**.

in Table 7. Through the investigation, we found that the reaction is sluggish than the alkenyl anion **9**, so 20 mol % of copper iodide was loaded to the reaction (compare the results in Table 3 with those in Table 7). Iodomethane and allyl iodide were applied as electrophiles, and the yields of the products were corresponding to the deuterium incorporation of the alkenyl anion **14** (entries 2 and 3).

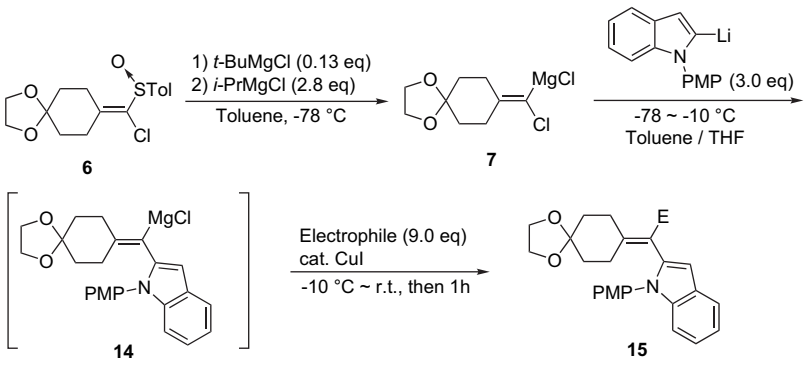
Also, the generality of this reaction was investigated by using 1-chlorovinyl *p*-tolyl sulfoxides, which were derived from cyclopentadecanone and cyclohexanone and the results are summarized in Table 8. The results show that this reaction could be generally applied to other 1-chlorovinyl *p*-tolyl sulfoxides though the yield remained somewhat low.

It is known that when bulky protective groups are on the nitrogen of indole, *C*-3 position will be lithiated.[12b] We investigated using *N*-TBS indole and *N*-TIPS indole,[15] which were synthesized by known procedure. *N*-Protected-3-lithio indole was prepared by known procedure, and was reacted with magnesium alkylidene carbenoid **7** (Scheme 5).

Through this study, we found out that *N*-TIPS indole gave better yield of the desired product than *N*-TBS indole though the yield turned out low. Alike the previous results in the alkenylation of 2-position of indole, no other product, which was alkenylated at the other position of the indole ring was obtained.

According to the previous study, we confirmed the existence of the alkenyl anion **18**, and applied several electrophiles to

Table 7. Trapping the intermediate **14** with electrophiles

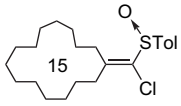
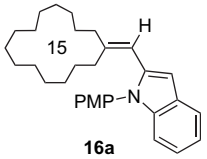
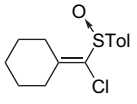
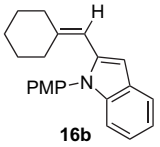


6 **7** **14** **15**

Entry	Electrophile	CuI/mol %	E	Yield of **15**/%
1	CH_3OD	None	–D	**15a**, 44[a]
2	CH_3I	20	$–CH_3$	**15b**, 33
3	$CH_3═CHCH_2I$	20	$–CH_2CH═CH_2$	**15c**, 30

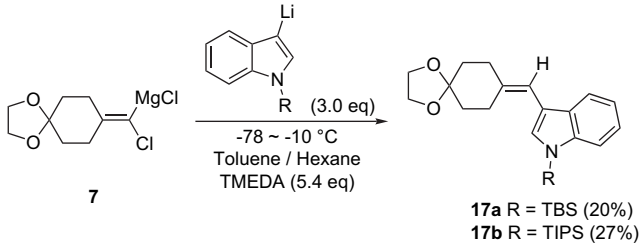
[a] Deuterium content 74%.

Table 8. Generality of substrates in the reaction between 1-chlorovinyl *p*-tolyl sulfoxide and *N*-PMP-2-lithio indole

Entry	1-Chlorovinyl *p*-tolyl sulfoxide	2-Alkenylated indole	Yield of **16**/%
1	 **11a**	 **16a**	34
2	 **11b**	 **16b**	30

react with the alkenyl anion **18**. The results are summarized in Table 9.

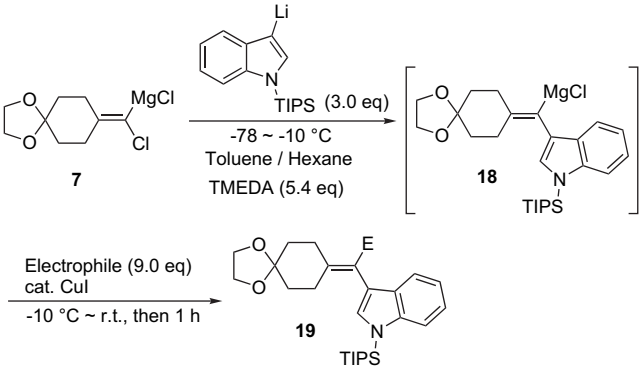
In conclusion, we developed a novel method for direct alkenylation of nitrogen-containing heterocycles at the nitrogen, *C*-2, and *C*-3 positions of the indole in a mild condition by the reaction of magnesium alkylidene carbenoid and lithiated nitrogen-containing heterocycles. Although the yields are not satisfactory by using this procedure, all of the intermediates could be trapped by electrophiles; which leads to the product having the alkenyl group fully substituted.



7

Scheme 5. Reaction of *N*-protected-3-lithio indole with magnesium alkylidene carbenoid **7**.

Table 9. Trapping the intermediate **18** with electrophiles



7 **18** **19**

Entry	Electrophile	CuI/mol %	E	Yield of **19**/%
1	CH_3OD	None	–D	**19a**, 27[a]
2	CH_3I	5	$–CH_3$	**19b**, 22
3	$CH_2═CHCH_2I$	5	$–CH_2CH═CH_2$	**19c**, 25

[a] Deuterium content 94%.

3. Experimental

3.1. General

All melting points were measured on a Yanaco MP-S3 apparatus and are uncorrected. ^1H NMR spectra were measured in a $CDCl_3$ solution with JEOL JNM-LA 300, 500, Bruker DPX 400, and AV 600 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion by HITACHI M-80B mass spectrometer. IR spectra were recorded on a Perkin–Elmer Spectrum One FTIR instrument. Silica gel 60 N (KANTO CHEMICAL) containing 0.5% fluorescence reagent 254 and a quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation. In experiments requiring a dry solvent and reagent, toluene, hexane, and HMPA were distilled from CaH_2 and THF, cyclopentyl methyl ether, diethyl ether, DME, and 1,4-dioxane were distilled from diphenylketyl.

3.1.1. 1-(1,4-Dioxa-spiro[4.5]dec-8-ylidenemethyl)-1*H*-indole (8a). To a solution of **6** (98.1 mg; 0.3 mmol) in 6 mL of dry toluene in a flame-dried flask at −78 °C under argon atmosphere was added *t*-BuMgCl (1.0 M solution in THF, 0.04 mL; 0.039 mmol) dropwise with stirring. After 10 min, *i*-PrMgCl (2.0 M solution in THF, 0.42 mL; 0.84 mmol) was added dropwise to the reaction mixture to give magnesium alkylidene carbenoid **7**. *n*-BuLi (1.6 M solution in hexane, 0.62 mL; 0.99 mmol) was added dropwise to a solution of indole (105.4 mg; 0.9 mmol) in 4 mL of dry toluene and dry diethyl ether (0.28 mL; 2.70 mmol) in an another flame-dried flask at −78 °C under argon atmosphere to give the *N*-lithio indole. This solution was added to the carbenoid **7** through a cannula. Temperature of the reaction mixture was gradually allowed to warm to −10 °C. The reaction was quenched by satd aq NH_4Cl and the whole was extracted three times with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The concentrate was purified by flash column chromatography (hexane/1,4-dioxane) to give **8a** (45.9 mg; 57%) as colorless crystals; mp 73–74 °C (hexane); IR (KBr) 3097, 2947, 1668, 1603, 1511, 1476, 1458, 1331, 1123, 1083, 904, 730 cm^{-1}; ^1H NMR δ 1.65 (2H, t, J=6.4 Hz), 1.84 (2H, t, J=6.4 Hz), 2.35 (2H, t, J=6.4 Hz), 2.45 (2H, t, J=6.4 Hz), 3.97–4.00 (4H, m), 6.55 (1H, d, J=3.1 Hz), 6.62 (1H, s), 7.06 (1H, d, J=3.2 Hz), 7.13 (1H, t, J=7.3 Hz), 7.21 (1H, t, J=7.4 Hz), 7.28 (1H, d, J=8.3 Hz), 7.62 (1H, d, J=7.9 Hz). MS m/z (%) 269 (M^+, 100), 224 (22), 208 (22), 196 (45), 182 (38), 168 (28), 154 (22), 130 (11), 117 (12), 99 (8), 89 (9), 77 (8). Calcd for $C_{17}H_{19}NO_2$: M, 269.1414. Found: m/z 269.1421. Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.00. Found: C, 75.59; H, 7.05; N, 5.19.

3.1.2. 1-(1,4-Dioxa-spiro[4.5]dec-8-ylidenemethyl)-1*H*-indazole (8b). Colorless oil; IR (neat) 2949, 1677, 1613, 1496, 1466, 1420, 1380, 1220, 1114, 1083, 1033 cm^{-1}; ^1H NMR δ 1.70 (2H, t, J=6.4 Hz), 1.86 (2H, t, J=6.4 Hz), 2.49 (2H, t, J=6.4 Hz), 2.54 (2H, t, J=6.4 Hz), 3.99–4.00 (4H, m), 6.80 (1H, s), 7.17 (1H, t, J=7.1 Hz), 7.34 (1H, d, J=8.6 Hz), 7.39 (1H, dd, J=12.4, 7.4 Hz), 7.74 (1H, d, J=8.3 Hz), 8.09 (1H, s). MS m/z (%) 270 (M^+, 49), 253 (19), 225 (20), 209 (12), 197 (22), 183 (46), 169 (22), 155 (9), 144 (7), 131 (100), 118 (10), 104 (17), 86 (16), 77 (13). Calcd for $C_{16}H_{18}N_2O_2$: M, 270.1371. Found: m/z 270.1369.

3.1.3. 1-(1,4-Dioxa-spiro[4.5]dec-8-ylidenemethyl)-1*H*-pyrazole (8c). Colorless oil; IR (neat) 2949, 1681, 1515, 1395, 1121, 1095, 1082, 1033, 906 cm^{-1}; ^1H NMR δ 1.71 (2H, t, J=6.4 Hz), 1.79 (2H, t, J=6.4 Hz), 2.41 (2H, t, J=6.4 Hz), 2.58 (2H, t, J=6.4 Hz), 3.98 (4H, s), 6.30–6.31 (1H, m), 6.69 (1H, s), 7.42 (1H, d, J=2.2 Hz), 7.59 (1H, s). MS m/z (%) 220 (M^+, 91), 219 (10), 194 (10), 175 (100), 159 (10), 147 (61), 133 (39), 119 (32), 99 (18), 81 (70), 79 (19), 53 (16). Calcd for $C_{12}H_{16}N_2O_2$: M, 220.1212. Found: m/z 220.1220.

3.1.4. 10-(1,4-Dioxa-spiro[4.5]dec-8-ylidenemethyl)-10*H*-phenothiazine (8d). Yellow crystals; mp 115–116 °C (AcOEt/hexane); IR (KBr) 2953, 1590, 1571, 1460, 1443, 1242, 1126, 1105, 1082, 1033, 902 cm^{-1}; ^1H NMR δ 1.58 (2H, t, J=6.4 Hz), 1.83 (2H, t, J=6.4 Hz), 2.35 (2H, t, J=6.4 Hz), 2.52 (2H, t, J=6.4 Hz), 3.96–3.95 (4H, m), 6.12 (1H, s), 6.81–6.86 (4H, m), 7.01–7.05 (4H, m). Anal. Calcd for $C_{21}H_{21}NSO_2$: C, 71.77; H, 6.02; N, 3.99; S, 9.12. Found: C, 71.72; H, 5.93; N, 4.02; S, 9.07.

3.1.5. 10-(1,4-Dioxa-spiro[4.5]dec-8-ylidenemethyl)-10*H*-phenoxazine (8e). Colorless crystals; mp 108–109 °C (hexane); IR (KBr) 2957, 1587, 1486, 1336, 1271, 1134, 1091 cm^{-1}; ^1H NMR δ 1.64 (2H, t, J=6.4 Hz), 1.83 (2H, t, J=6.4 Hz), 2.30 (2H, t, J=6.4 Hz), 2.50 (2H, t, J=6.4 Hz), 3.93–3.99 (4H, m), 5.50 (1H, s), 6.44 (2H, d, J=7.9 Hz), 6.64–6.67 (4H, m), 6.70–6.75 (2H, m). Anal. Calcd for $C_{21}H_{21}NO_3$: C, 75.20; H, 6.31; N, 4.18. Found: C, 75.27; H, 6.33; N, 4.14.

3.1.6. 1-(1,4-Dioxa-spiro[4.5]dec-8-ylidenemethyl)-1*H*-pyrrole (8f). Colorless oil; IR (neat) 2949, 1677, 1488, 1121, 1091 cm^{-1}; ^1H NMR δ 1.67 (2H, t, J=6.4 Hz), 1.77 (2H, t, J=6.4 Hz), 2.36 (2H, t, J=6.4 Hz), 2.43 (2H, t, J=6.4 Hz), 3.98 (4H, s), 6.19 (2H, m), 6.53 (1H, s), 6.65 (2H, m). MS m/z (%) 219 (M^+, 100), 174 (20), 158 (9), 146 (62), 132 (51), 118 (28), 104 (9), 80 (9), 77 (8), 53 (9). Calcd for $C_{13}H_{17}NO_2$: M, 219.1257. Found: m/z 219.1255.

3.1.7. 2-(1,4-Dioxa-spiro[4.5]dec-8-ylidenemethyl)-1*H*-pyrrole (8g). Purple oil; IR (neat) 3368 (NH), 2950, 2885, 1688, 1435, 1374, 1250, 1118, 1081, 1032, 906 cm^{-1}; ^1H NMR δ 1.72 (2H, t, J=6.4 Hz), 1.76 (2H, t, J=6.4 Hz), 2.40 (2H, dt, J=6.1, 1.2 Hz), 2.64 (2H, dt, J=6.5, 1.0 Hz), 3.99 (4H, m), 6.04 (1H, s), 6.16 (1H, br s), 6.22 (1H, m), 6.72 (1H, m), 8.02 (1H, br s). MS m/z (%) 219 (M^+, 100), 190 (10), 174 (30), 158 (30), 156 (15), 132 (16), 118 (32), 99 (68), 93 (12), 80 (28), 55 (13). Calcd for $C_{13}H_{17}NO_2$: M, 219.1259. Found: m/z 219.1254.

3.1.8. 1-(1,4-Dioxa-spiro[4.5]dec-8-ylidenemethyl)-2,5-dimethyl-1*H*-pyrrole (8h). Yellow oil; IR (neat) 2950, 2885, 1668, 1521, 1436, 1408, 1377, 1122, 1084, 1033, 908 cm^{-1}; ^1H NMR δ 1.61 (2H, t, J=6.4 Hz), 1.79 (2H, t, J=6.4 Hz), 2.07 (6H, s), 2.08 (2H, t, J=6.4 Hz), 2.44 (2H, t, J=6.4 Hz), 3.97–3.98 (4H, m), 5.79 (2H, s), 6.16 (1H, s). MS m/z (%) 247 (M^+, 100), 202 (22), 174 (28), 160 (67), 132 (13), 86 (12), 77 (10), 53 (11). Calcd for $C_{15}H_{21}NO_2$: M, 247.1571. Found: m/z 247.1573.

3.1.9. 10-[1-(1,4-Dioxa-spiro[4.5]dec-8-ylidene)-ethyl]-10*H*-phenothiazine (10b). To a solution of **6** (98.1 mg; 0.3 mmol) in 6 mL of dry toluene in a flame-dried flask at −78 °C under argon atmosphere was added *t*-BuMgCl (1.0 M solution in THF, 0.04 mL; 0.039 mmol) dropwise with stirring. After 10 min, *i*-PrMgCl (2.0 M solution in THF, 0.42 mL; 0.84 mmol) was added dropwise to give the magnesium alkylidene carbenoid **7**. *n*-BuLi (1.6 M solution in hexane, 0.62 mL; 0.99 mmol) was added dropwise to a solution of phenothiazine (179.3 mg; 0.9 mmol) in 4 mL of dry toluene and dry diethyl ether (0.28 mL; 2.70 mmol) in an another flame-dried flask at −78 °C under argon atmosphere to give the *N*-lithio phenothiazine. This solution was added to the carbenoid **7** through a cannula. Temperature of the reaction mixture was gradually allowed to warm to −10 °C. Copper iodide (2.9 mg; 0.015 mmol) was added to the reaction mixture and was stirred for 10 min. Then, iodomethane (0.17 mL; 2.70 mmol) was added dropwise to the reaction mixture. The reaction mixture was gradually allowed to

warm to 0 °C, and then was stirred for 1 h at room temperature. The reaction was quenched by satd aq NH_4Cl and the whole was extracted three times with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The concentrate was purified by flash column chromatography (hexane/AcOEt) to give **10b** (68.3 mg; 62%) as colorless crystals; mp 125–126 °C (hexane); IR (KBr) 2962, 1590, 1565, 1461, 1299, 1238, 1126, 1099 cm^{-1}; ^1H NMR δ 1.60 (2H, t, J=6.4 Hz), 1.83 (2H, t, J=6.4 Hz), 1.91 (3H, s), 2.29 (2H, t, J=6.4 Hz), 2.55 (2H, t, J=6.4 Hz), 3.92–3.99 (4H, m), 6.46 (2H, dd, J=8.2, 1.3 Hz), 6.70 (2H, dt, J=7.4, 1.3 Hz), 6.82 (2H, dd, J=7.5, 1.5 Hz), 6.88 (2H, dt, J=7.3, 1.5 Hz). Anal. Calcd for $C_{22}H_{23}NSO_2$: C, 72.30; H, 6.34; N, 3.83; S, 8.77. Found: C, 72.28; H, 6.31; N, 3.79; S, 8.81.

3.1.10. 10-[1-(1,4-Dioxa-spiro[4.5]dec-8-ylidene)-propyl]-10*H*-phenothiazine (10c). Colorless crystals; mp 113–114 °C (hexane); IR (KBr), 2959, 1592, 1570, 1457, 1442, 1307, 1238, 1097, 1030 cm^{-1}; ^1H NMR δ 1.05 (3H, t, J=7.7 Hz), 1.64 (2H, t, J=6.4 Hz), 1.87 (2H, t, J=6.4 Hz), 2.14 (2H, t, J=6.4 Hz), 2.40 (2H, q, J=7.7 Hz), 2.62 (2H, t, J=6.4 Hz), 3.93–4.00 (4H, m), 6.54 (2H, d, J=8.2 Hz), 6.73 (2H, t, J=7.5 Hz), 6.86–6.91 (4H, m). Anal. Calcd for $C_{23}H_{25}NSO_2$: C, 72.79; H, 6.64; N, 3.69; S, 8.45. Found: C, 72.85; H, 6.49; N, 3.66; S, 8.36.

3.1.11. 10-[1-(1,4-Dioxa-spiro[4.5]dec-8-ylidene)-but-3-enyl]-10*H*-phenothiazine (10d). Yellow crystals; mp 79–80 °C (hexane); IR (KBr) 2957, 1591, 1570, 1457, 1442, 1302, 1239, 1124, 1089, 900 cm^{-1}; ^1H NMR δ 1.65 (2H, t, J=6.4 Hz), 1.87 (2H, t, J=6.4 Hz), 2.18 (2H, t, J=6.4 Hz), 2.64 (2H, t, J=6.4 Hz), 3.14 (2H, d, J=7.0 Hz), 3.93–4.00 (4H, m), 4.90 (1H, dd, J=11.0, 1.3 Hz), 5.09 (1H, dd, J=15.6, 1.2 Hz), 5.77–5.83 (1H, m), 6.53 (2H, d, J=7.9 Hz), 6.73 (2H, t, J=7.3 Hz), 6.85–6.90 (4H, m). Anal. Calcd for $C_{24}H_{25}NSO_2$: C, 73.62; H, 6.44; N, 3.58. Found: C, 73.63; H, 6.29; N, 3.78.

3.1.12. 10-[1-(1,4-Dioxa-spiro[4.5]dec-8-ylidene)-2-phenylethyl]-10*H*-phenothiazine (10e). Yellow oil; IR (neat), 3062, 2952, 1738, 1593, 1572, 1461, 1370, 1308, 1239, 1124, 1092, 1043, 943, 897 cm^{-1}; ^1H NMR δ 1.67 (2H, t, J=6.4 Hz), 1.96 (2H, t, J=6.4 Hz), 2.15 (2H, t, J=6.4 Hz), 2.87 (2H, t, J=6.4 Hz), 3.63 (2H, s), 3.95–4.03 (4H, m), 6.36 (2H, dd, J=8.1, 0.9 Hz), 6.66 (2H, dt, J=7.4, 1.0 Hz), 6.74 (2H, dt, 7.6, 1.5 Hz), 6.82 (2H, dd, J=7.4, 1.8 Hz), 6.98–7.00 (1H, m), 7.06 (2H, t, J=7.1 Hz), 7.29 (2H, d, J=7.4 Hz). MS m/z 441 (M^+, 100), 411 (1), 397 (2), 350 (7), 326 (1), 306 (3), 264 (11), 249 (2), 236 (4), 198 (21), 167 (4), 128 (4), 115 (3), 99 (8), 91 (6), 55 (3). Calcd for $C_{28}H_{27}NSO_2$: M, 441.1762. Found: m/z 441.1753.

3.1.13. 2-(1,4-Dioxa-spiro[4.5]dec-8-ylidene)-2-phenothiazin-10-yl-1-phenyl-ethanone (10f). To a solution of **6** (98.1 mg; 0.3 mmol) in 6 mL of dry toluene in a flame-dried flask at −78 °C under argon atmosphere was added *t*-BuMgCl (1.0 M solution in THF, 0.04 mL; 0.039 mmol) dropwise with stirring. After 10 min, *i*-PrMgCl (2.0 M solution in THF, 0.42 mL; 0.84 mmol) was added dropwise to give the magnesium alkylidene carbenoid **7**. *n*-BuLi (1.6 M solution in hexane, 0.62 mL; 0.99 mmol) was added dropwise to a solution of phenothiazine (179.3 mg; 0.9 mmol) in 4 mL of dry toluene and dry diethyl ether (0.28 mL; 2.70 mmol) in an another flame-dried flask at −78 °C under argon atmosphere to give the *N*-lithio phenothiazine. This solution was added to the carbenoid **7** through a cannula. Temperature of the reaction mixture was gradually allowed to warm to −10 °C. Then, benzoyl chloride (0.31 mL; 2.70 mmol) was added dropwise to the reaction mixture. The reaction mixture was gradually allowed to warm to 0 °C, and then was stirred for 1 h at room temperature. The reaction was quenched by satd aq NH_4Cl and the whole was washed with 5% aq NaOH, extracted three times with $CHCl_3$ and the organic layer was neutralized by satd aq NH_4Cl. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The concentrate was purified by flash column chromatography (hexane/AcOEt) to give **10f** (81.2 mg; 59%) as orange crystals; mp 145–146 °C (AcOEt/hexane); IR (KBr) 2953, 1655 (CO), 1593, 1461, 1444, 1237, 1122, 1092, 1032 cm^{-1}; ^1H NMR δ 1.77 (2H, t, J=6.4 Hz), 1.85 (2H, t, J=6.4 Hz), 2.57 (2H, t, J=6.4 Hz), 2.61 (2H, t, J=6.4 Hz), 3.96 (4H, br s), 6.76 (2H, d, J=8.3 Hz), 6.83 (2H, t, J=7.6 Hz), 6.93–6.95 (2H, m), 6.99 (2H, dt, J=8.3, 0.9 Hz), 7.36 (2H, t, J=7.7 Hz), 7.51 (1H, t, J=7.0 Hz), 7.82 (2H, d, J=7.4 Hz). Anal. Calcd for $C_{28}H_{25}NSO_3$: C, 73.82; H, 5.53; N, 3.07; S, 7.04. Found: C, 73.59; H, 5.37; N, 3.03; S, 6.97.

3.1.14. 2-(1,4-Dioxa-spiro[4.5]dec-8-ylidene)-2-phenothiazin-10-yl-*N*-phenyl-acetamide (10g). To a solution of **6** (98.1 mg; 0.3 mmol) in 6 mL of dry toluene in a flame-dried flask at −78 °C under argon atmosphere was added *t*-BuMgCl (1.0 M solution in THF, 0.04 mL; 0.039 mmol) dropwise with stirring. After 10 min, *i*-PrMgCl (2.0 M solution in THF, 0.42 mL; 0.84 mmol) was added dropwise to give the magnesium alkylidene carbenoid **7**. *n*-BuLi (1.6 M solution in hexane, 0.62 mL; 0.99 mmol) was added dropwise to a solution of phenothiazine (179.3 mg; 0.9 mmol) in 4 mL of dry toluene and dry diethyl ether (0.28 mL; 2.70 mmol) in an another flame-dried flask at −78 °C under argon atmosphere to give the *N*-lithio phenothiazine. This solution was added to the carbenoid **7** through a cannula. Temperature of the reaction mixture was gradually allowed to warm to −10 °C. Then, phenyl isocyanate (0.29 mL; 2.70 mmol) was added dropwise to the reaction mixture. The reaction mixture was gradually allowed to warm to 0 °C, and then was stirred for 1 h at room temperature. The reaction was quenched by satd aq NH_4Cl and the whole was extracted three times with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The concentrate was purified by flash column chromatography (hexane/AcOEt) to give **10g** (55.7 mg; 39%) as colorless crystals; mp 157–158 °C (AcOEt/hexane); IR (KBr) 3366 (NH), 2968, 2887, 1669 (CO), 1599, 1513, 1459, 1436, 1309, 1236, 1187, 1125, 1111, 1088, 1032, 944, 906 cm^{-1}; ^1H NMR δ 1.79 (2H, t, J=6.5 Hz), 2.01 (2H, t, J=6.7 Hz), 2.46 (2H, t, J=6.5 Hz), 3.57 (2H, t, J=6.7 Hz), 3.97–4.05 (4H, m), 6.68 (2H, dd, J=8.2, 1.0 Hz), 6.91 (2H, dt, J=7.3, 1.2 Hz), 7.01–7.27 (5H, m), 7.24–7.27 (2H, m), 7.49 (2H, dd, J=8.7, 1.2 Hz), 8.8 (1H, s). Anal. Calcd for $C_{28}H_{26}N_2SO_3$: C, 71.47; H, 5.57; N, 5.95; S, 6.81. Found: C, 71.539; H, 5.40; N, 5.93; S, 6.75.

3.1.15. 1-Cyclopentadecylidenemethyl-1*H*-indole (12a). Colorless oil; IR (neat) 2927, 2856, 1662, 1611, 1510,

1461, 1322, 1234, 1122, 1088, 1010 cm^{-1}; ^1H NMR δ 1.23–1.51 (22H, m), 1.59 (2H, quintet, J=7.7 Hz), 2.08 (2H, t, J=7.7 Hz), 2.23 (2H, t, J=7.3 Hz), 6.53 (1H, d, J=3.4 Hz), 6.55 (1H, s), 7.06 (1H, d, J=3.1 Hz), 7.11 (1H, t, J=7.3 Hz), 7.19 (1H, t, J=8.0 Hz), 7.26 (1H, d, J=8.0 Hz), 7.61 (1H, d, J=8.0 Hz). MS m/z 337 (M^+, 100), 336 (16), 294 (8), 280 (3), 252 (3), 238 (4), 210 (4), 182 (14), 168 (22), 156 (12), 117 (28), 95 (4), 81 (4), 55 (6). Calcd for $C_{24}H_{35}N$: M, 337.2767. Found: m/z 337.2771.

3.1.16. 1-Cyclohexylidenemethyl-1*H*-indole (12b). Colorless oil; IR (neat); 2928, 2853, 1511, 1476, 1462, 1318, 1233 cm^{-1}; ^1H NMR δ 1.49–1.53 (2H, m), 1.58–1.66 (2H, m), 1.67–1.72 (2H, m), 2.15 (2H, t, J=6.1 Hz), 2.30 (2H, t, J=5.7 Hz), 6.53 (2H, d, J=1.8 Hz), 7.04–7.06 (1H, m), 7.09–7.13 (1H, m), 7.20 (1H, dt, J=7.0, 1.5 Hz), 7.27–7.29 (1H, m), 7.61 (1H, dd, J=7.9, 1.0 Hz). MS m/z 211 (M^+, 100), 183 (28), 168 (38), 154 (20), 130 (17), 117 (51), 95 (8), 89 (10), 77 (11), 63 (6). Calcd for $C_{15}H_{17}N$: M, 211.1360. Found: m/z 211.1363.

3.1.17. 1-(2-Methyl-propenyl)-1*H*-indole (12c). Colorless oil; IR (neat) 3051, 2914, 1679, 1610, 1510, 1462, 1325, 1224 cm^{-1}; ^1H NMR δ 1.69 (3H, s), 1.91 (3H, s), 6.54 (1H, d, J=3.1 Hz), 6.57 (1H, t, J=1.3 Hz), 7.08–7.13 (2H, m), 7.18–7.21 (1H, m), 7.26 (1H, d, J=8.3 Hz), 7.62 (1H, d, J=7.6 Hz). MS m/z 171 (M^+, 100), 156 (48), 130 (25), 117 (10), 89 (9), 77 (8). Calcd for $C_{12}H_{13}N$: M, 171.1046. Found: m/z 171.1042.

3.1.18. (*E*)-1-Cyclohex-2-enylidenemethyl-1*H*-indole (12d). Colorless oil; IR (neat) 3029, 2925, 2854, 1729, 1641, 1614, 1514, 1461, 1323, 1312, 1247, 1199 cm^{-1}; ^1H NMR δ 1.71 (2H, quintet, J=6.1 Hz), 2.19 (2H, m), 2.50 (2H, dt, J=6.3, 1.6 Hz), 5.95 (1H, dt, J=10.1, 4.3 Hz), 6.28 (1H, dt, J=9.8, 1.8 Hz), 6.58 (1H, d, J=3.1 Hz), 6.70 (1H, s), 7.14 (1H, t, J=7.5 Hz), 7.20 (1H, d, J=3.1 Hz), 7.23 (1H, t, J=7.6 Hz), 7.33 (1H, d, J=8.3 Hz), 7.62 (1H, d, J=8.0 Hz). MS m/z 209 (M^+, 100), 194 (12), 180 (14), 167 (10), 154 (10), 130 (13), 117 (21), 91 (21), 77 (18), 63 (19). Calcd for $C_{15}H_{15}N$: M, 209.1203. Found: m/z 209.1208.

3.1.19. (*Z*)-1-Cyclohex-2-enylidenemethyl-1*H*-indole (12e). Colorless oil; IR (neat) 3032, 2927, 2857, 1645, 1610, 1513, 1461, 1316, 1199, 1121 cm^{-1}; ^1H NMR δ 1.83–1.88 (2H, m), 2.22–2.24 (2H, m), 2.49–2.52 (2H, m), 5.91–5.97 (1H, m), 6.29–6.31 (1H, m), 6.52 (1H, s), 6.56 (1H, d, J=3.4 Hz), 7.13 (1H, t, J=7.5 Hz), 7.18 (1H, d, J=3.1 Hz), 7.21 (1H, t, J=7.6 Hz), 7.31 (1H, d, J=8.2 Hz), 7.62 (1H, d, J=7.9 Hz). MS m/z 209 (M^+, 100), 194 (11), 180 (20), 167 (10), 154 (10), 130 (15), 117 (21), 91 (21), 77 (19), 63 (8). Calcd for $C_{15}H_{15}N$: M, 209.1204. Found: m/z 209.1205.

3.1.20. (*E*)-1-(2-Methyl-buta-1,3-dienyl)-1*H*-indole (12f). Colorless oil; IR (neat) 2924, 1645, 1515, 1461, 1321, 1249, 1199 cm^{-1}; ^1H NMR δ 1.94 (3H, d, J=1.0 Hz), 5.20 (1H, d, J=10.7 Hz), 5.35 (1H, d, J=17.4 Hz), 6.58–6.63 (2H, m), 6.93 (1H, br s), 7.16 (1H, t, J=7.9 Hz), 7.21–7.25 (2H, m), 7.32 (1H, d, J=8.0 Hz), 7.63 (1H, dd, J=7.9, 0.6 Hz). MS m/z 182 (M^+, 100), 167 (20), 89 (8), 77 (7). Calcd for $C_{13}H_{13}N$: M, 183.1047. Found: m/z 183.1041.

3.1.21. (*Z*)-1-(2-Methyl-buta-1,3-dienyl)-1*H*-indole (12g). Colorless oil; IR (neat) 2926, 1645, 1514, 1473, 1323, 1215 cm^{-1}; ^1H NMR δ 2.03 (3H, d, J=1.3 Hz), 5.20 (1H, dt, J=11.0, 1.5 Hz), 5.39 (1H, d, J=17.4 Hz), 6.58 (1H, dd, J=3.2, 0.9 Hz), 6.66 (1H, ddd, J=17.4, 10.4, 0.6 Hz), 6.74 (1H, s), 7.13–7.17 (2H, m), 7.22 (1H, dt, J=7.1, 1.2 Hz), 7.30 (1H, dd, J=8.1, 0.6 Hz), 7.62 (1H, d, J=7.9 Hz). MS m/z 182 (M^+, 100), 167 (19), 89 (7). Calcd for $C_{13}H_{13}N$: M, 183.1047. Found: m/z 183.1051.

3.1.22. (*E*)-1-(2-Phenyl-propenyl)-1*H*-indole (12h). Colorless oil; IR (neat) 3053, 3031, 2922, 1645, 1514, 1460, 1325, 1227 cm^{-1}; ^1H NMR δ 2.19 (3H, d, J=1.3 Hz), 6.63 (1H, d, J=6.7 Hz), 7.15 (1H, d, J=1.3 Hz), 7.17 (1H, d, J=7.9 Hz), 7.24 (1H, t, J=5.5 Hz), 7.27 (1H, d, J=3.1 Hz), 7.35 (2H, t, J=7.0 Hz), 7.41 (2H, t, J=8.0 Hz), 7.54 (2H, d, J=7.6 Hz), 7.65 (1H, d, J=7.9 Hz). MS m/z 234 (20), 233 (M^+, 100), 217 (18), 130 (14), 115 (20), 103 (18), 89 (12), 77 (12), 63 (9), 51 (11). Calcd for $C_{17}H_{15}N$: M, 233.1204. Found: m/z 233.1205.

3.1.23. (*Z*)-1-(2-Phenyl-propenyl)-1*H*-indole (12i). Colorless oil; IR (neat) 3054, 2918, 1659, 1515, 1461, 1323, 1200 cm^{-1}; ^1H NMR δ 2.24 (3H, d, J=1.5 Hz), 6.32 (1H, d, J=3.4 Hz), 6.62 (1H, d, J=3.4 Hz), 6.91 (1H, d, J=1.2 Hz), 7.11–7.14 (3H, m), 7.18–7.24 (4H, m), 7.41 (1H, dd, J=8.3, 0.9 Hz), 7.60 (1H, d, J=7.6 Hz). MS m/z 234 (20), 233 (M^+, 100), 217 (19), 130 (15), 115 (22), 102 (9), 89 (9), 77 (11), 63 (7), 51 (11). Calcd for $C_{17}H_{15}N$: M, 233.1203. Found: m/z 233.1200.

3.1.24. (*E*)-1-(2-Methyl-hept-1-enyl)-1*H*-indole (12j). Colorless oil; IR (neat) 3053, 2928, 2856, 1729, 1671, 1511, 1461, 1322 cm^{-1}; ^1H NMR δ 0.94 (3H, t, J=7.0 Hz), 1.34–1.42 (4H, m), 1.54–1.60 (2H, m), 1.68 (3H, d, J=1.2 Hz), 2.22 (2H, dt, J=7.3, 0.7 Hz), 6.54–6.55 (1H, m), 6.58–6.59 (1H, m), 7.09–7.13 (2H, m), 7.19–7.22 (1H, m), 7.25 (1H, dd, J=8.2, 0.9 Hz), 7.62 (1H, d, J=8.0 Hz). MS m/z 227 (M^+, 51), 184 (9), 170 (100), 154 (19), 130 (9), 117 (12), 41 (8). Calcd for $C_{16}H_{21}N$: M, 227.1673. Found: m/z 227.1675.

3.1.25. (*Z*)-1-(2-Methyl-hept-1-enyl)-1*H*-indole (12k). Colorless oil; IR (neat) 2956, 2926, 2857, 1462, 1324 cm^{-1}; ^1H NMR δ 0.81 (3H, t, J=7.0 Hz), 1.13–1.24 (4H, m), 1.37–1.44 (2H, m), 1.90 (3H, d, J=1.5 Hz), 2.06 (2H, t, J=7.7 Hz), 6.53–6.54 (2H, m), 7.05 (1H, d, J=3.1 Hz), 7.11 (1H, t, J=7.5 Hz), 7.19 (1H, dt, J=7.0, 1.2 Hz), 7.27 (1H, d, J=8.2 Hz), 7.62 (1H, d, J=7.9 Hz). MS m/z 227 (M^+, 52), 184 (9), 170 (100), 154 (19), 130 (10), 117 (15), 41 (7). Calcd for $C_{16}H_{21}N$: M, 227.1673. Found: m/z 227.1675.

3.1.26. (*E*)-1-(2-Methyl-4-phenyl-but-1-enyl)-1*H*-indole (12l). Colorless oil; IR (neat) 3026, 2923, 1510, 1461, 1323 cm^{-1}; ^1H NMR δ 1.74 (3H, d, J=0.9 Hz), 2.54 (2H, t, J=7.9 Hz), 2.89 (2H, t, J=7.4 Hz), 6.50 (1H, d, J=1.2 Hz), 6.53 (1H, d, J=3.4 Hz), 7.04–7.06 (2H, m), 7.10 (1H, t, J=7.3 Hz), 7.17 (1H, dt, J=7.0, 0.9 Hz), 7.24 (3H, d, J=7.1 Hz), 7.33 (2H, t, J=7.6 Hz), 7.60 (1H, dd, J=7.8, 0.9 Hz). MS m/z 261 (M^+, 27), 170 (100), 154 (15), 91 (8). Calcd for $C_{19}H_{19}N$: M, 261.1516. Found: m/z 261.1525.

3.1.27. (*Z*)-1-(2-Methyl-4-phenyl-but-1-enyl)-1*H*-indole (12m). Colorless oil; IR (neat) 3027, 2927, 1510, 1461, 1324, 1221 cm^{-1}; ^1H NMR δ 1.96 (3H, d, J=1.2 Hz), 2.38 (2H, t, J=8.6 Hz), 2.72 (2H, t, J=7.6 Hz), 6.49 (1H, d, J=3.1 Hz), 6.56 (1H, d, J=1.0 Hz), 6.82 (1H, d, J=3.1 Hz), 7.02–7.04 (2H, m), 7.09–7.17 (2H, m), 7.18–7.22 (4H, m), 7.61 (1H, d, J=7.9 Hz). MS m/z 261 (M^+, 28), 170 (100), 154 (15), 91 (8). Calcd for $C_{19}H_{19}N$: M, 261.1516. Found: m/z 261.1512.

3.1.28. 2-(1,4-Dioxa-spiro[4.5]dec-8-ylidenemethyl)-1-methyl-1*H*-indole (13a). To a solution of **6** (98.1 mg; 0.3 mmol) in 6 mL of dry THF in a flame-dried flask at −78 °C under argon atmosphere was added *t*-BuMgCl (1.0 M solution in THF, 0.04 mL; 0.039 mmol) dropwise with stirring. After 10 min, *i*-PrMgCl (2.0 M solution in THF, 0.42 mL; 0.84 mmol) was added dropwise to give the magnesium alkylidene carbenoid **7**. *n*-BuLi (1.6 M solution in hexane, 0.62 mL; 0.99 mmol) was added dropwise to a solution of *N*-methyl indole (231.6 mg; 0.9 mmol) in 4 mL of dry THF in an another flame-dried flask at room temperature under argon atmosphere and was stirred for 30 min to give the 2-lithio *N*-methyl indole. This solution was cooled to −78 °C and was added to the carbenoid **7** through a cannula. Temperature of the reaction mixture was gradually allowed to warm to −10 °C. The reaction was quenched by satd aq NH_4Cl and the whole was extracted three times with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The concentrate was purified by flash column chromatography (hexane/AcOEt) to give **13a** (17.1 mg; 20%) as colorless crystals; mp 107–108 °C (hexane); IR (KBr) 2950, 2877, 1656, 1530, 1465, 1360, 1334, 1314, 1244, 1229, 1123, 1079, 1030 cm^{-1}; ^1H NMR δ 1.71 (2H, t, J=6.7 Hz), 1.83 (2H, t, J=6.7 Hz), 2.51 (2H, dt, J=6.6, 1.3 Hz), 2.65 (2H, dt, J=6.6, 1.3 Hz), 3.67 (3H, s), 3.99–4.00 (4H, m), 6.21 (1H, s), 6.36 (1H, s), 7.07 (1H, dt, J=7.9, 0.9 Hz), 7.17 (1H, dt, J=8.3, 1.2 Hz), 7.27 (1H, dd, J=8.7, 0.9 Hz), 7.56 (1H, d, J=7.9 Hz). Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.47; N, 4.94. Found: C, 76.14; H, 7.46; N, 4.91.

3.1.29. 1-Benzenesulfonyl-2-(1,4-dioxa-spiro[4.5]dec-8-ylidenemethyl)-1*H*-indole (13b). To a solution of **6** (98.1 mg; 0.3 mmol) in 6 mL of dry THF in a flame-dried flask at −78 °C under argon atmosphere was added *t*-BuMgCl (1.0 M solution in THF, 0.04 mL; 0.039 mmol) dropwise with stirring. After 10 min, *i*-PrMgCl (2.0 M solution in THF, 0.42 mL; 0.84 mmol) was added dropwise to give the magnesium alkylidene carbenoid **7**. *n*-BuLi (1.6 M solution in hexane, 0.62 mL; 0.99 mmol) was added dropwise to a solution of 1-benzenesulfonyl indole (231.6 mg; 0.9 mmol) in 4 mL of dry THF in an another flame-dried flask at −78 °C under argon atmosphere to give the 2-lithio *N*-benzenesulfonyl indole. This solution was added to the carbenoid **7** through a cannula. Temperature of the reaction mixture was gradually allowed to warm to −10 °C. The reaction was quenched by satd aq NH_4Cl and the whole was extracted three times with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The concentrate was purified by flash column chromatography (hexane/AcOEt) to give **13b** (40.6 mg; 33%) as colorless oil; IR (neat) 3065, 2950, 2883, 1646, 1585, 1473, 1448, 1372, 1225, 1173, 1150, 1034, 905 cm^{-1}; ^1H NMR δ 1.49 (2H, t, J=6.3 Hz), 1.80 (2H, t, J=6.2 Hz), 2.35 (2H, t, J=5.8 Hz), 2.51 (2H, t, J=5.8 Hz), 3.94–4.02 (4H, m), 6.34 (1H, s), 6.61 (1H, s), 7.23 (1H, dt, J=7.8, 1.0 Hz), 7.28–7.32 (1H, m), 7.34–7.38 (2H, m), 7.43 (1H, d, J=7.8 Hz), 7.47–7.51 (1H, m), 7.71 (2H, m), 8.25 (1H, d, J=8.5 Hz). MS m/z 409 (M^+, 80), 347 (3), 323 (13), 268 (62), 224 (17), 206 (27), 182 (100), 167 (48), 117 (24), 99 (24), 77 (36), 55 (10). Calcd for $C_{23}H_{23}NSO_4$: M, 409.1356. Found: m/z 409.1352.

3.1.30. 2-(1,4-Dioxa-spiro[4.5]dec-8-ylidenemethyl)-indole-1-carboxylic acid *tert*-butyl ester (13c). Colorless crystals; mp 112–113 °C (hexane); IR 2940, 1735 (CO), 1456, 1361, 1333, 1159, 1117, 1097 cm^{-1}; ^1H NMR δ 1.65 (9H, s), 1.71 (2H, t, J=6.2 Hz), 1.81 (2H, t, J=6.5 Hz), 2.48 (2H, t, J=6.5 Hz), 2.59 (2H, t, J=6.5 Hz), 3.99 (4H, br s), 6.35 (1H, s), 6.44 (1H, s), 7.18–7.27 (2H, m), 7.48 (1H, d, J=7.8 Hz), 8.14 (1H, d, J=8.3 Hz). Anal. Calcd for $C_{22}H_{27}NO_4$: C, 71.52; H, 7.37; N, 3.79. Found: C, 71.56; H, 7.39; N, 3.75.

3.1.31. 2-(1,4-Dioxa-spiro[4.5]dec-8-ylidenemethyl)-1-(2-trimethylsilanyloxy-ethyl)-1*H*-indole (13d). To a solution of **6** (98.1 mg; 0.3 mmol) in 6 mL of dry THF in a flame-dried flask at −78 °C under argon atmosphere was added *t*-BuMgCl (1.0 M solution in THF, 0.04 mL; 0.039 mmol) dropwise with stirring. After 10 min, *i*-PrMgCl (2.0 M solution in THF, 0.42 mL; 0.84 mmol) was added dropwise to give the magnesium alkylidene carbenoid **7**. *n*-BuLi (1.6 M solution in hexane, 0.62 mL; 0.99 mmol) was added dropwise to a solution of 1-SEM indole (0.23 mL; 0.9 mmol) in 4 mL of dry THF in an another flame-dried flask at 0 °C under argon atmosphere and was stirred for 30 min to give the 2-lithio *N*-SEM indole. The solution was cooled to −78 °C and added to the carbenoid **7** through a cannula. Temperature of the reaction mixture was gradually allowed to warm to −10 °C. The reaction was quenched by satd aq NH_4Cl and the whole was extracted three times with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The concentrate was purified by flash column chromatography (hexane/1,4-dioxane) to give **13d** (17.5 mg; 15%) as colorless oil; IR (neat) 2950, 2887, 1652, 1538, 1460, 1311, 1248, 1116, 1081, 1034, 910, 859 cm^{-1}; ^1H NMR δ −0.07 (9H, s), 0.87 (2H, t, J=8.0 Hz), 1.71 (2H, t, J=6.8 Hz), 1.82 (2H, t, J=6.5 Hz), 2.51 (2H, t, J=6.6 Hz), 2.66 (2H, t, J=6.5 Hz), 3.49 (2H, t, J=8.0 Hz), 4.00 (4H, br s), 5.47 (1H, s), 6.31 (1H, s), 6.39 (1H, s), 7.10 (1H, dt, J=7.0, 0.3 Hz), 7.18 (1H, ddd, J=7.3, 7.0, 0.3 Hz), 7.42 (1H, d, J=8.3 Hz), 7.55 (1H, d, J=7.8 Hz). MS m/z 399 (M^+, 100), 369 (1), 341 (1), 311 (8), 282 (31), 281 (24), 255 (14), 220 (8), 196 (26), 182 (15), 167 (11), 130 (4), 99 (10), 73 (45). Calcd for $C_{23}H_{33}NO_3Si$: M, 399.2230. Found: m/z 399.2231.

3.1.32. 2-(1,4-Dioxa-spiro[4.5]dec-8-ylidenemethyl)-1-(4-methoxy-phenyl)-1*H*-indole (13e). To a solution of **6** (98.1 mg; 0.3 mmol) in 6 mL of dry toluene in a flame-dried flask at −78 °C under argon atmosphere was added *t*-BuMgCl (1.0 M solution in THF, 0.04 mL; 0.039 mmol) dropwise with stirring. After 10 min, *i*-PrMgCl (2.0 M solution in THF, 0.42 mL; 0.84 mmol) was added dropwise to give the magnesium alkylidene carbenoid **7**. *n*-BuLi (1.6 M solution in hexane, 0.62 mL; 0.99 mmol) was added

dropwise to a solution of *N*-PMP indole (401.9 mg; 0.9 mmol) in 4 mL of dry THF in an another flame-dried flask at room temperature under argon atmosphere and was stirred for 1 h to give the 2-lithio *N*-PMP indole. This solution was cooled to −78 °C and was added to the carbenoid **7** through a cannula. Temperature of the reaction mixture was gradually allowed to warm to −10 °C. The reaction was quenched by satd aq NH_4Cl and the whole was extracted three times with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The concentrate was purified by flash column chromatography (hexane/1,4-dioxane) to give **13d** (49.7 mg; 44%) as colorless crystals; mp 107–108 °C (hexane); IR (KBr) 2949, 1515, 1494, 1461, 1247, 1232, 1123, 1081, 1031 cm^{-1}; ^1H NMR δ 1.70 (2H, t, *J*=6.4 Hz), 1.81 (2H, t, *J*=6.5 Hz), 2.48 (2H, t, *J*=7.3 Hz), 2.49 (2H, t, *J*=7.4 Hz), 3.88 (3H, s), 3.94–3.99 (4H, m), 6.33 (1H, s), 6.64 (1H, d, *J*=3.0 Hz), 6.97 (1H, d, *J*=8.8 Hz), 7.15 (1H, t, *J*=6.9 Hz), 7.20 (1H, t, *J*=6.9 Hz), 7.25 (1H, d, *J*=2.8 Hz), 7.27 (1H, d, *J*=3.0 Hz), 7.31 (1H, dd, *J*=8.8, 2.5 Hz), 7.47 (1H, d, *J*=8.3 Hz), 7.68 (1H, d, *J*=8.0 Hz). Anal. Calcd for $C_{24}H_{25}NO_3$: C, 76.77; H, 6.71; N, 3.73. Found: C, 76.72; H, 6.67; N, 3.70.

3.1.33. 2-[1-(1,4-Dioxa-spiro[4.5]dec-8-ylidene)-ethyl]-1-(4-methoxy-phenyl)-1*H*-indole (15b). Colorless oil; IR (neat) 2950, 1524, 1496, 1459, 1249, 1127, 1096, 1033 cm^{-1}; ^1H NMR δ 1.60–1.66 (2H, m), 1.74–1.80 (2H, m), 1.97 (3H, s), 2.13–2.15 (2H, m), 2.46–2.51 (2H, m), 3.85 (3H, s), 3.96–3.97 (4H, m), 6.54 (1H, d, *J*=3.0 Hz), 6.99 (1H, d, *J*=8.8 Hz), 7.14–7.16 (2H, m), 7.18–7.22 (1H, m), 7.28–7.33 (2H, m), 7.47 (1H, d, *J*=8.0 Hz), 7.67 (1H, d, *J*=7.6 Hz). MS *m*/*z* 389 (M^+, 100), 344 (8), 303 (12), 288 (21), 250 (5), 103 (21), 86 (7). Calcd for $C_{25}H_{27}NO_3$: *M*, 389.1990. Found: *m*/*z* 389.1996.

3.1.34. 2-[1-(1,4-Dioxa-spiro[4.5]dec-8-ylidene)-but-3-enyl]-1-(4-methoxy-phenyl)-1*H*-indole (15c). Colorless oil; IR (neat) 2950, 1610, 1514, 1496, 1458, 1248, 1228, 1125, 1033, 943 cm^{-1}; ^1H NMR δ 1.61–1.81 (4H, m), 2.14–2.18 (2H, m), 2.45–2.52 (2H, m), 2.99 (1H, dd, *J*=15.3, 6.8 Hz), 3.27 (1H, dd, *J*=15.4, 6.0 Hz), 3.85 (3H, s), 3.96–3.98 (4H, m), 4.88–5.01 (2H, m), 5.67–5.80 (1H, m), 6.64 (1H, dd, *J*=3.3, 0.8 Hz), 6.98 (1H, d, *J*=9.0 Hz), 7.10–7.21 (3H, m), 7.27 (1H, d, *J*=3.3 Hz), 7.32 (1H, dd, *J*=8.7, 2.5 Hz), 7.46 (1H, d, *J*=8.3 Hz), 7.67 (1H, d, *J*=8.0 Hz). MS *m*/*z* 415 (M^+, 100), 375 (13), 374 (11), 329 (11), 314 (11), 288 (7), 286 (3), 236 (3), 204 (3), 192 (2), 180 (2), 165 (2), 99 (5), 86 (2). Calcd for $C_{27}H_{29}NNO_3$: *M*, 415.2147. Found: *m*/*z* 415.2138.

3.1.35. 2-Cyclopentadecylidenemethyl-1-(4-methoxy-phenyl)-1*H*-indole (16a). Colorless oil; IR (neat) 2927, 2856, 1609, 1584, 1514, 1495, 1460, 1292, 1248, 1229, 1215, 1034 cm^{-1}; ^1H NMR δ 1.34–1.58 (26H, m), 2.26 (2H, dt, *J*=14.1, 7.5 Hz), 3.88 (3H, s), 6.34 (1H, s), 6.65 (1H, d, *J*=3.3 Hz), 6.95–7.32 (6H, m), 7.50 (1H, d, *J*=8.3 Hz), 7.68 (1H, d, *J*=8.0 Hz). MS *m*/*z* 443 (M^+, 100), 442 (3), 400 (2), 386 (1), 358 (1), 316 (1), 274 (4), 236 (5), 206 (2), 204 (1), 159 (2), 145 (1), 116 (1). Calcd for $C_{31}H_{41}NO$: *M*, 443.3188. Found: *m*/*z* 443.3187.

3.1.36. 2-Cyclohexylidenemethyl-1-(4-methoxy-phenyl)-1*H*-indole (16b). Colorless oil; IR (neat) 2927, 2852, 1652, 1608, 1585, 1514, 1495, 1456, 1335, 1291, 1247, 1122, 1033 cm^{-1}; ^1H NMR δ 1.57–1.66 (7H, m), 2.33 (3H, dt, *J*=15.1, 6.0 Hz), 3.89 (3H, s), 6.26 (1H, s), 6.65 (1H, d, *J*=3.3 Hz), 6.95–7.04 (2H, m), 7.07–7.22 (2H, m), 7.24–7.30 (2H, m), 7.49 (1H, d, *J*=8.3 Hz), 7.68 (1H, d, *J*=7.3 Hz). MS *m*/*z* 317 (M^+, 100), 236 (11), 206 (8). Calcd for $C_{22}H_{23}NO$: *M*, 317.1777. Found: *m*/*z* 317.1776.

3.1.37. 1-(*tert*-Butyl-dimethyl-silanyl)-3-(1,4-dioxa-spiro[4.5]dec-8-ylidenemethyl)-1*H*-indole (17a). To a solution of **6** (98.1 mg; 0.3 mmol) in 6 mL of dry toluene in a flame-dried flask at −78 °C under argon atmosphere was added *t*-BuMgCl (1.0 M solution in THF, 0.04 mL; 0.039 mmol) dropwise with stirring. After 10 min, *i*-PrMgCl (2.0 M solution in THF, 0.42 mL; 0.84 mmol) was added dropwise to give the magnesium alkylidene carbenoid **7**. *t*-BuLi (1.6 M solution in pentane, 0.86 mL; 1.35 mmol) was added dropwise to a solution of *N*-TBS indole (208.3 mg; 0.9 mmol) in 4 mL of dry hexane and dry TMEDA (0.24 mL; 1.62 mmol) in an another flame-dried flask at 0 °C under argon atmosphere to give the 3-lithio *N*-TBS indole. This solution was cooled to −78 °C and was added to the carbenoid **7** through a cannula. Temperature of the reaction mixture was gradually allowed to warm to −10 °C. The reaction was quenched by satd aq NH_4Cl and the whole was extracted three times with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The concentrate was purified by flash column chromatography (hexane/1,4-dioxane) to give **17a** (23.3 mg; 57%) as colorless oil; IR (neat) 2951, 2883, 2858, 1606, 1539, 1463, 1471, 1452, 1311, 1257, 1142, 1074, 960 cm^{-1}; ^1H NMR δ 0.59 (6H, s), 0.93 (9H, s), 1.70 (2H, t, *J*=6.3 Hz), 1.82 (2H, t, *J*=6.5 Hz), 2.51 (2H, t, *J*=6.5 Hz), 2.57 (2H, t, *J*=6.5 Hz), 3.96–4.01 (4H, m), 6.34 (1H, s), 7.04 (1H, s), 7.10–7.18 (2H, m), 7.46–7.48 (1H, m), 7.57–7.59 (1H, m). MS *m*/*z* 383 (M^+, 100), 354 (1), 322 (10), 282 (3), 244 (3), 240 (8), 208 (5), 174 (4), 167 (4), 130 (2), 99 (3), 73 (14). Calcd for $C_{23}H_{33}NO_2Si$: *M*, 383.2278. Found: *m*/*z* 383.2273.

3.1.38. 3-(1,4-Dioxa-spiro[4.5]dec-8-ylidenemethyl)-1-triisopropylsilanyl-1*H*-indole (17b). Yellow oil; IR (neat) 2948, 2869, 1606, 1541, 1450, 1141, 1120, 1074 cm^{-1}; ^1H NMR δ 1.14 (18H, d, *J*=7.6 Hz), 1.63–1.73 (5H, m), 1.82 (2H, t, *J*=6.4 Hz), 2.51 (2H, t, *J*=6.3 Hz), 2.59 (2H, t, *J*=6.4 Hz), 3.98 (4H, s), 6.36 (1H, s), 7.10–7.17 (3H, m), 7.47 (1H, d, *J*=7.1 Hz), 7.59 (1H, d, *J*=6.5 Hz). MS *m*/*z* 425 (M^+, 100), 424 (2), 382 (4), 364 (4), 339 (4), 296 (5), 280 (3), 268 (2), 230 (2), 208 (3), 180 (2), 167 (2), 153 (1), 115 (4), 73 (5), 59 (7). Calcd for $C_{29}H_{39}NO_2Si$: *M*, 425.2750. Found: *m*/*z* 425.2746.

3.1.39. 3-[1-(1,4-Dioxa-spiro[4.5]dec-8-ylidene)-ethyl]-1-triisopropylsilanyl-1*H*-indole (19b). Colorless oil; IR (neat) 2927, 2869, 1605, 1544, 1449, 1212, 1135, 1096, 1035, 943 cm^{-1}; ^1H NMR δ 1.14 (18H, d, *J*=7.5 Hz), 1.59 (2H, t, *J*=6.5 Hz), 1.69 (3H, septet, *J*=7.5 Hz), 1.80 (2H, t, *J*=6.5 Hz), 2.06 (3H, s), 2.25 (2H, t, *J*=6.0 Hz), 2.54 (2H, t, *J*=6.3 Hz), 3.96–4.01 (4H, m), 6.97 (1H, s), 7.07–7.15 (2H, m), 7.46 (1H, d, *J*=7.0 Hz), 7.48 (1H, d, *J*=7.6 Hz). MS *m*/*z* 439 (M^+, 100), 425 (6), 396 (8), 394 (6), 352 (5), 310 (6), 294 (4), 282 (3), 230 (2), 222 (6), 196 (2), 167 (2), 157 (1), 115 (4), 73 (5). Calcd for $C_{27}H_{41}NO_2Si$: *M*, 439.2901. Found: *m*/*z* 439.2904.

3.1.40. 3-[1-(1,4-Dioxa-spiro[4.5]dec-8-ylidene)-butyl]-1-triisopropylsilanyl-1*H*-indole (19c). Colorless oil; IR (neat) 2947, 2869, 1634, 1606, 1542, 1463, 1449, 1366, 1211, 1135, 1096, 1034, 1015, 954 cm^{-1}; ^1H NMR δ 1.13 (18H, d, J=7.5 Hz), 1.60 (2H, t, J=6.8 Hz), 1.68 (3H, septet, J=7.5 Hz), 1.80 (2H, t, J=6.3 Hz), 2.23 (2H, t, J=6.8 Hz), 2.53 (2H, t, J=6.8 Hz), 3.17 (2H, d, J=6.3 Hz), 3.92–4.00 (4H, m), 4.90 (1H, dd, J=7.0, 2.0 Hz), 4.95 (1H, dd, J=17.2, 2.0 Hz), 5.76 (1H, ddt, J=16.9, 12.6, 6.5 Hz), 6.96 (1H, s), 7.08 (1H, dt, J=7.0, 1.3 Hz), 7.13 (1H, dt, J=7.0, 1.5 Hz), 7.46 (2H, t, J=7.8 Hz). MS m/z 465 (M^+, 100), 464 (3), 425 (15), 424 (14), 378 (3), 336 (4), 308 (2), 292 (1), 248 (4), 222 (2), 208 (2), 180 (1), 157 (1), 115 (5), 87 (4). Calcd for $C_{29}H_{43}NO_2Si$: M, 465.3063. Found: m/z 465.3067.

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